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Micropatterning of Multiple Photonic Colloidal Crystal Gels for Flexible Structural Color Films

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ABSTRACT

We herein report the micropatterning of flexible multiple photonic colloidal crystal gels (PCCGs) using single-layered microchannels. These patterned PCCGs exhibit structural colors that can be tuned by adjustment of the diameter and concentration of the colloidal particles in precursor solutions of *N*-isopropylacrylamide (NIPAM) or polyethylene glycol diacrylate (PEGDA). The precursor solutions containing dispersed colloidal particles were selectively injected into single-layered microchannels where they polymerized rapidly. The shape, density, and height of the patterned PCCG pixels were determined by the microchannels, which in turn determined the optical properties of the PCCG arrays. Furthermore, the preparation of three different types of PCCGs exhibiting three different structural colors at a high pixel density was demonstrated successfully using the single-layered polydimethylsiloxane (PDMS) microchannels. Finally, the optical reflective properties and the mechanical flexibility of the patterned multiple PCCG arrays were evaluated. We expected that our method for the preparation of such patterned PCCG arrays will contribute to the development of flexible optical devices.

INTRODUCTION

Colloidal suspensions, composed of a dispersion of colloidal particles (1 nm to 1 μm in diameter) within a liquid have received growing interest from both scientists and engineers because of the unique relationship between their microscopic phenomena and their behavior. Upon balancing the attractive/repulsive interactions between colloidal particles, such as electrostatic[1,2] and magnetic forces[3,4], the particles can arrange in a regular manner and diffract specific wavelengths of light as indicated by Bragg's law. In particular, suspended colloidal crystals in polymer solutions diffract light at visible wavelengths. This is known as structural color, and allows the application of such systems in the area of photonics, more specifically as optical colored materials[5–8], biosensors, and chemical sensors[9–12]. Among the various systems reported to date, photonic colloidal crystal gels (PCCGs), where colloidal particles with diameters of hundreds of nanometers are regularly arranged in a polymer gel network, have attracted particular attention because of their structural colors, which can be tuned by altering the swell-shrink behavior of the polymer gel network[1,13]. As such, the features of these PCCGs can be precisely controlled by simply changing the size and geometry of the colloidal particles, and so can be maintained while the structure remains intact. Furthermore, flexibility can be imparted on the PCCGs, as the embedded colloidal particles in the gel network are not in direct contact with one another.

Through adaptation of the various characteristics of PCCGs, it is expected that a flexible, light weight and mechanically robust optical filter could be developed for flexible display applications[8,14]. However, to apply PCCGs as flexible optical filters, the micropatterning of multiple types of PCCGs (i.e., to give basic colors, such as red, green, and blue) is necessary. In previous work, a micropatterning method for PCCGs using inkjet printing was reported,[15–17] in which multiple types of dome-shaped PCCGs were patterned on a flexible sheet at a resolution of several micrometers. However, this method did not allow control of the shape

and thickness of the patterned PCCG dots, as the patterned shape and thickness of the droplets injected from the inkjet nozzle were determined by the fluid characteristics of the droplets and the hydrophobicity of the printing substrate. In addition, the pixel density was relatively low (13% of the whole area)[15], as it was necessary to introduce gaps to prevent mixing of the adjacent liquids. However, since the optical pixel element for a flexible structural color film must be combined with various circuits for screen switching, control of the shape and thickness to determine the resolution and optical characteristics is necessary.

Thus, we herein propose a selective and rapid micropatterning method for the preparation of multiple types of PCCG using a single-layered microchannel (**Figure 1(a)**). Using our proposed method, we expect to achieve thickness control (**Figure 1(b)**) and dense patterning of various shapes (**Figure 1(c)**), thus leading to multiple types of PCCGs in a single-layered microchannel, due to the effect of the internal microchannel shape. A mixture of a colloidal suspension in *N*-isopropylacrylamide (NIPAM) or polyethylene glycol diacrylate (PEGDA) will be employed as the precursor. Using these colloidal polymer suspensions, we aim to demonstrate a multi-colored pixel-patterned PCCG flexible structural color film in a thin polydimethylsiloxane (PDMS) microchannel and subsequent evaluation of its optical characteristics.

MATERIALS AND METHODS

Preparation of Colloidal Precursor Solution: For preparation of the desalted colloidal precursors, aqueous solutions of the monomer (1 M, NIPAM (095-03692, Wako Pure Chemical Industries, Ltd.)), crosslinker (0.1 M, BIS (134-02352, Wako Pure Chemical Industries, Ltd.)) and photoinitiator (1 vol%, IRGACURE1173, BASF) were mixed with a desalted monodisperse silica colloidal suspension to give silica concentrations between 0.48 and 0.08 g/mL (particle diameter: 110 nm and 180 nm (MP-1040 and MP-2040 Nissan

Chemical Industries, Ltd.)). These precursors were then desalted once again over 30 min using ion exchange resin (AG501-X8, BIO-RAD). After desalting, nitrogen was bubbled through the precursor suspensions for 10 min, prior to their injection into microchannels.

Microchannel preparation: The microchannel masters were prepared on glass slides (Matsunami, S9112). Initially, the glass slides were cleaned with acetone, isopropyl alcohol and ethanol, and heated to dryness on a hot plate at 95°C. The dried glass slides where then coated with a negative photoresist (SU-8 3050 or SU-8 3025, MicroChem) using a spin coater for 30 s, where the thickness of the photoresist layer was controlled by the rotation speed. To prepare the 25 and 60 μm thick photoresist layers, SU-8 3025 was applied at a rotation speed of either 3000 or 1200 rpm, while to prepare the 110 μm thick photoresist layers, SU-8 3050 was applied at 1500 rpm. The coated glass slides were then placed on a hotplate at 95°C for 1 h and exposed to UV light using a designed photomask for 20 s. The glass slide was then heated once again at 95°C for 5 min, after which time the photoresist layer was developed using SU-8 developer (MicroChem). Subsequently, the microchannels were prepared by soft lithography. A mixture of the PDMS (SILPOT 184, Dow Corning Toray Co., Ltd.) base material and curing agent was poured onto the master and heated on a hotplate at 75°C for 1.5 h. After removal of the cured PDMS replica from the master by peeling, the replica was bonded to a PDMS sheet after oxygen plasma treatment.

Micropatterning of three types of PCCGs: Microchannels were prepared containing three downstream branches of the tournament and three different lengths of flow path. Note that each microchannel was treated with the photoinitiator solution (2 vol%) for 1 h before injecting colloidal precursor solution. The longest channels were opened by cutting the end of the microchannel, and the first colloidal precursor was injected into the open channels (silica concentration: 0.48 g/mL, particle diameter: 180 nm). After curing the precursor by exposure to UV light (AS One, HLR100T-2) for 1.5 min, the tournament shape area was covered by

aluminum foil. Subsequently, the next longest channels were opened and the remaining mixture was removed by suction. The second colloidal mixture (silica concentration: 0.36 g/mL, particle diameter: 180 nm) was then injected into the open channels and exposed to UV light for 1.5 min. Finally, the shortest channels were opened, the third precursor was injected into the open channels (silica concentration: 0.24g/mL, particle diameter: 110 nm), and the precursor was cured by exposure to UV light for 1.5 min.

Characterization of PCCGs: The reflection spectra of the samples were measured by using an Olympus, BX-50 light microscope equipped with a UV-Vis-NIR spectrometer (Ocean Optics, USB2000+) and an Olympus U-LH100 light source. The patterned PCCGs and microchannels were also observed using a digital microscope (Keyence, VH-Z20R).

RESULTS AND DISCUSSION

As mentioned previously, PCCGs exhibit structural colors due to the regular arrangement of desalted colloidal particles and their solidification through polymerization. In general, the repulsion of the electrostatic double layer at the surface of desalted colloidal particles determines the distance between the particles. When the particles arrange regularly, the volume fraction of the particles is 74%. Therefore, a pseudo particle diameter, D (which is the total of all particle diameters plus the thickness of the electrostatic double layer), can be calculated from the volume fraction, f_p, and the diameter of the colloidal particles, D_p:

$$D = D_p \sqrt[3]{0.74 / f_p} \quad (1)$$

In addition, the wavelength of the light reflected from PCCGs is dependent on the refractive index, the angle of incident light, θ, and the structural period of the material. In this context, the refractive index can be determined from the fraction of the colloidal particles and the gel, f_p and f_g, and refractive indices of the colloidal particles and the gel, n_p and n_g, as per Bragg's law:[18,19]

$$m\lambda = 2D\sqrt{\frac{2}{3}}\sin\theta\sqrt{f_p n_p^2 + f_g n_g^2} \quad (2)$$

We herein prepared desalted colloidal precursors composed of NIPAM and a colloidal silica suspension, where the silica particle concentration was between 0.48 and 0.08 g/mL, and the diameters of the colloidal particles were 110 and 180 nm. After treatment of the microchannel with the IRGACURE photoinitiator (2 vol%) for 1 h to cure the various holes and corners of microchannel (**Figure SI1**), the colloidal precursor solutions were injected into the microchannel (width: 200 μm, thickness: 110 μm) and cured to form gels (Figures 2(a-i) and 2(a-ii)). Vertical reflection spectra of the PCCGs in the microchannel were then recorded, and it was found that the cured PCCGs exhibited structural colors, except when a silica concentration of 0.08 g/mL was employed. The peak wavelength of reflection spectra of PCCGs, where the silica particle concentration was 0.32 g/mL and diameters of the colloidal particles were 110 and 180 nm, were 404 nm and 668 nm, respectively. These values were substituted into Equation 1 and 2 to obtain the calculated peak wavelength. Note that the particles in the PCCGs for our experiments could be regularly arranged in short range but could be amorphous-like aggregate state in long range[20], based on angle dependency measurement (**Figure SI2**). Thus, the equation 2 could just be used as an indicator for the short-range crystal structures. As shown **Table 1**, the peak wavelengths of the PCCGs in the visible range varied from 404 to 668 nm. However, at a silica concentration <0.08g/mL, the interparticle distance could not be maintained, and the regular ordered structure required for structural colors to be exhibited disappeared. In addition, at low concentrations and with large particle diameters, the peak wavelength of the reflected light was red-shifted, due to the increased interparticle distance. This result indicated that the structural colors of PCCGs can be tuned by varying the concentrations and diameters of the colloidal particles.

To examine the effect of PCCG thickness on the reflected light, we prepared three types of microchannels (width: 200 μm in all cases) with thicknesses of 25, 70 and 110 μm. These

microchannels were deaerated in the presence of a photoinitiator for 1 h, and the desalted colloidal precursors were injected into the microchannels and cured under UV light over 1.5 min to give a silica concentration of 0.48 g/mL and a particle diameter of 180 nm. **Figure 2(b)** shows the top and cross-sectional views of the crystallized PCCGs in the microchannels, which confirmed that the PCCGs were tightly packed in the microchannels regardless of the PCCG thickness. These PCCGs exhibited a green structural color, and the vertical reflection spectra confirmed that the peak reflectance of these patterned PCCGs occurred at approximately 560 nm in all cases (**Figure 2(c)**). Although sharp peaks were observed for all PCCGs, the signal intensities were found to depend on the thickness of the PCCGs. When the PCCG thickness is <110 μm, thicker PCCGs reflected more light, thus resulting in a more intense signal. This result indicated that variation in the thickness of such materials can control the optical properties of the patterned PCCGs.

To pattern multiple types of PCCGs at high pixel densities, we modified our previously reported channel-cut method[21] to utilize photo-curable PCCGs. The microchannels reported herein were composed of pixel diameters of 300μm, channels widths and thicknesses of 100 and 50μm, respectively, and different channel lengths for each group (**Figure 3(a-i)**). The microchannels were prepared from two PDMS layers that were synthesized via a standard photolithography technique,[21] followed by treatment of the microchannel wall with a photoinitiator for 1 h. The resulting PDMS microchannels (**Figure 3(a-ii))** contained a 20 mm-by-20 mm pixel array.

The initial step in patterning multiple types of PCCGs in the microchannels involved, opening the longest microchannels via cutting then injecting the first precursor solution containing the suspended colloidal particles (concentration:0.24 g/mL, paticle diameter: 110 nm) into only the open ended channels (**Figure 3(b-i)**). In this case, the precursor solution, which initially exhibited a blue structural color, was an aqueous solution containing the

NIPAM monomer (1 M), the *N,N′*-methylene-bis-acrylamide crosslinker (BIS, 0.1 M), and the IRGACURE photoinitiator. The injected precursor solution was then cured by exposure to UV irradiation for 1.5 min (**Figures 3(b-ii) and 4(a)**), during which the tournament area was covered by aluminum foil to avoid gelation in this area. The closed channels were then cut open and the remaining uncured suspension was removed by suction prior to preparation of the subsequent PCCG pattern (**Figure 3(b-iii)**).

The second colloidal precursor (particle concentration: 0.48 g/ml, diameter: 180 nm) was then injected into the microchannels through selective introduction into only the shorter open channels (**Figures 3(b-iv) and 4(b)**), as the longer channels had been previously filled with the first colloidal precursor. Following UV exposure for 1.5 min, the second cured PCCGs exhibited a green structural color. As a result, we succeeded in patterning two different types of PCCG in a single-layered microchannel at a high pixel density (61.0%). Furthermore, we also note that this micropatterning method is not limited by the type of hydrogel material, as we also succeeded in patterning polyethylene glycol (PEG)-based PCCGs in the microchannels (**Figure SI3**).

As the number of different types of patterned PCCGs in a flexible substrate can be determined by the number of downstream branches, we demonstrated the patterning of three different types of PCCGs in a microchannel containing three downstream branches (**Figure 5(a)**). Particle concentrations of 0.24, 0.36, and 0.48 g/mL, and particle diameters of 110, 180, and 180 nm, were employed for this purpose. We also found that the pixel shapes and PCCGs densities could be controlled, as three types of PCCGs were successfully patterned in microchannels containing quadrangular prism-shaped pixels (**Figure 5(b)**) and hexagonal cylindrical pixels (**Figure 5(c)**). In these case, the diagonal lengths of the pixels were 300 μm and the channel width were 100 μm. This result indicates that our patterning method can be applied to microchannels of various shapes. Furthermore, we confirmed that the pixel

densities achieved in these systems, i.e., the ratios of the areas occupied by PCCGs of circular pixels (61.0%), quadrangular prism-shaped pixels (66.6%) or hexagonal cylindrical pixels (78.9%) were significantly higher than those reported previously in the literature [15,16] (**Figure SI4**).

The vertical reflection spectra of the PCCGs were then measured, and sharp peaks corresponding to blue, green, and red structural colors were observed at 426, 554, and 600 nm, respectively (**Figure 5(d)**). This indicated that the ordered structure of the colloidal particles did not collapse even following multiple exposures to UV light. We therefore expect that additional types of PCCGs can be patterned in microchannels using our described method.

The flexibility of our patterned PCCG microarray was then confirmed by carrying out bending tests on the 20 mm-by-20 mm PCCG array (thickness: 2 mm) (Figure 6(a)). Bending of the patterned PCCG in the middle of the array was repeated 30 times (curvature: 3.5 mm-1) in directions parallel and perpendicular to the microchannels (Figure 6(a)). Figure 6(c) shows that the peak position in the reflection spectra of the PCCG remained constant both before and after bending. Furthermore, no cracking or breakage was observed in the bent PCCG, thus indicating that the patterned PCCGs could potentially be employed in flexible device applications.

The fabricated PCCGs can be applied as a color filter of a monochrome reflective display by simply put on the top of the display. An additional feature of our multicolored flexible structural color film is the ability to tune its optical properties by targeted microchannel design. Although there is the limitation of pattern design in our method since all pixels must be connected with channels for introducing colloidal polymer suspension, easiness of our patterning method that can be applied to multiple-types of PCCGs just by using a single-layered microchannel could be an advantage for fabricating multi-patterned PCCGs for

practical uses. In this study, we employed microchannels with a rectangular cross-section that had been prepared by photolithography, and the thickness, width, and pixel density of the microchannels were varied through photomask design during the fabrication process. In addition to our method, 3D printing technologies, which have significantly advanced in recent years, could allow the creation of channels with inclined or curved surfaces over a large area. Such surfaces could potentially control the optical properties of each pixel more precisely, in particular in the context of angle dependency,[20,22] which is a key factor to permit the practical application of optical devices using PCCGs.

We successfully demonstrated the patterning of multiple types of PGGGs in approximately 20 mm-by-20 mm area. On the other hand, some regions of the patterned PCCGs in the microchannel did not exhibit structural colors uniformly. This non-uniformity could be due to the effect of flows in the microchannel[2]. In our experiment, we manually introduced the colloidal polymer suspensions into the blanched microchannel by using a syringe without precise flow control, which could cause the difference of crystal formation inside the microchannel. Previous literature[2] shows that applying pulse-like pressure for introducing colloidal suspension improved the uniformity of the colloidal crystals in microchannels. This approach may contribute to improve the quality of PCCGs in our experiments.

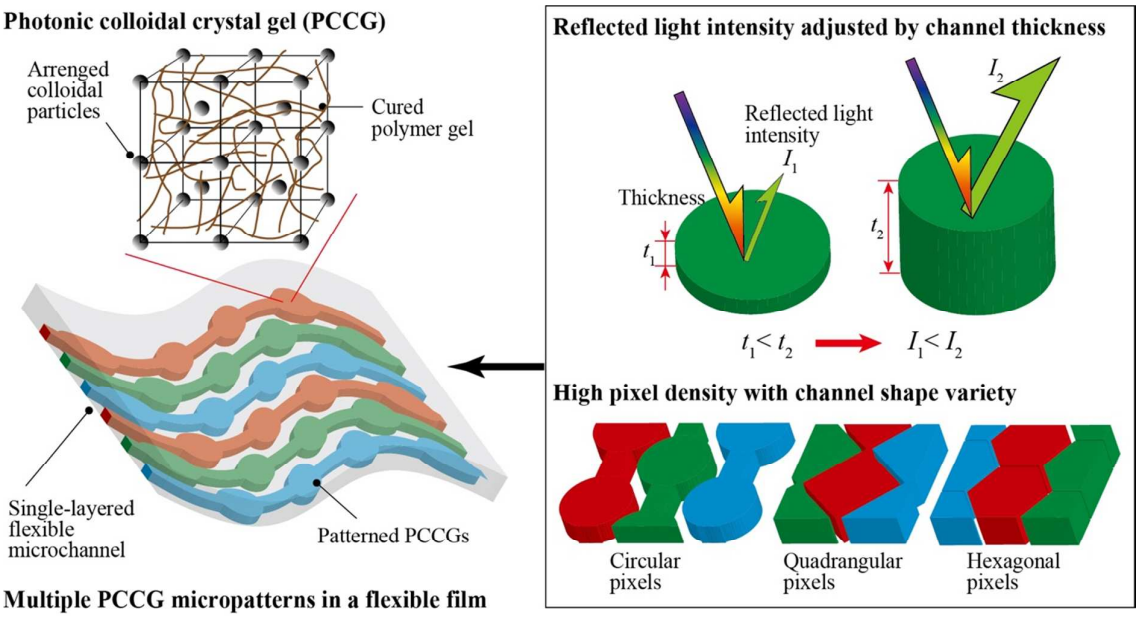
Previously, the preparation of multiple photonic colloidal crystals with high pattern densities by microfabrication techniques and subsequent curing using a photocurable polymer was reported[23]. However, this patterned photonic colloidal crystal contained rigid polymers and so did not exhibit flexibility. The use of a hydrogel as a structural color material can therefore enable the preparation of flexible and mechanically robust optical elements that are compatible with emerging highly flexible electronic[24] or optical devices[25]. However, the evaporation of water from the hydrogel present in the PCCG array must be solved, as this can

lead to changes in the desired structural colors. As such, sealing technologies[26,27] or the use of non-volatile liquids[28] instead of water may be necessary.

In addition to optical device applications, the use of hydrogel-based structural color elements could also lead to biochemical sensor applications, as stimuli-responsive hydrogels can swell-shrink in response to various biochemical substances[12,29]. Combining such sensor hydrogels with our multi-array technology will be expected to aid in the development of flexible optical-biochemical sensor arrays, which would be of particular interest for continuous environmental and healthcare monitoring systems.

CONCLUSIONS

To summarize, we succeeded in the preparation of flexible multiple PCCGs using single-layered microfluidic channel patterns. The structural colors and optical reflection properties exhibited by these patterned PCCGs were tuned by varying the concentration and diameter of the colloidal particles in the precursor solutions and modification of the microchannel geometries. Using this technology, flexible and highly dense pixel arrays with multiple colors have been demonstrated. We therefore expect that our micropatterning method for PCCGs could enhance the functionality of future flexible optical devices and biochemical sensors.



Multiple PCCG micropatterns in a flexible film

Figure 1. Schematic illustration of multiple types of patterned PCCGs in a single-layered flexible microchannel. Reflected light intensity of PCCG pixels can be adjusted by the thickness of the microchannel. Various shapes/patterns of PCCGs can be obtained by designing the shape of microchannel for achieving high pixel density.

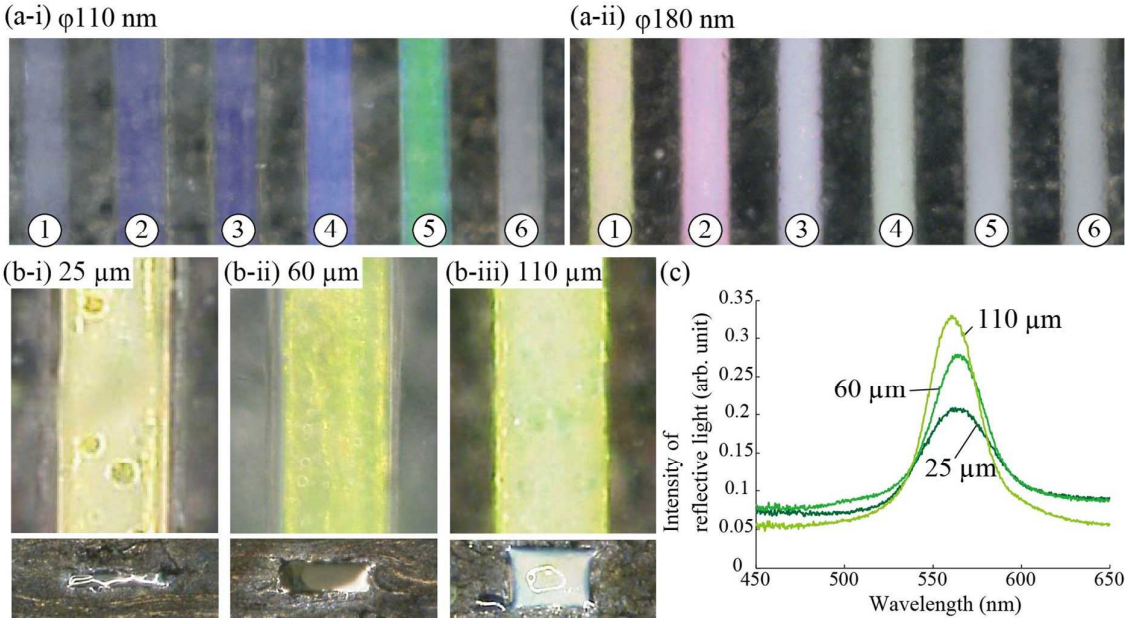


Figure 2. (a) Images showing the structural colors of the PCCGs at different silica particle concentrations (i.e., 0.48 and 0.08 mg/mL) with diameters of (a-i) 110 nm and (a-ii) 180 nm. (b) Top and cross-sectional views of the PCCGs in the microchannels with thicknesses of (b-i) 25 μm, (b-ii) 60 μm and (b-iii) 110 μm. (c) Reflection spectra of the PCCGs with thicknesses of 25, 60, and 110 μm.

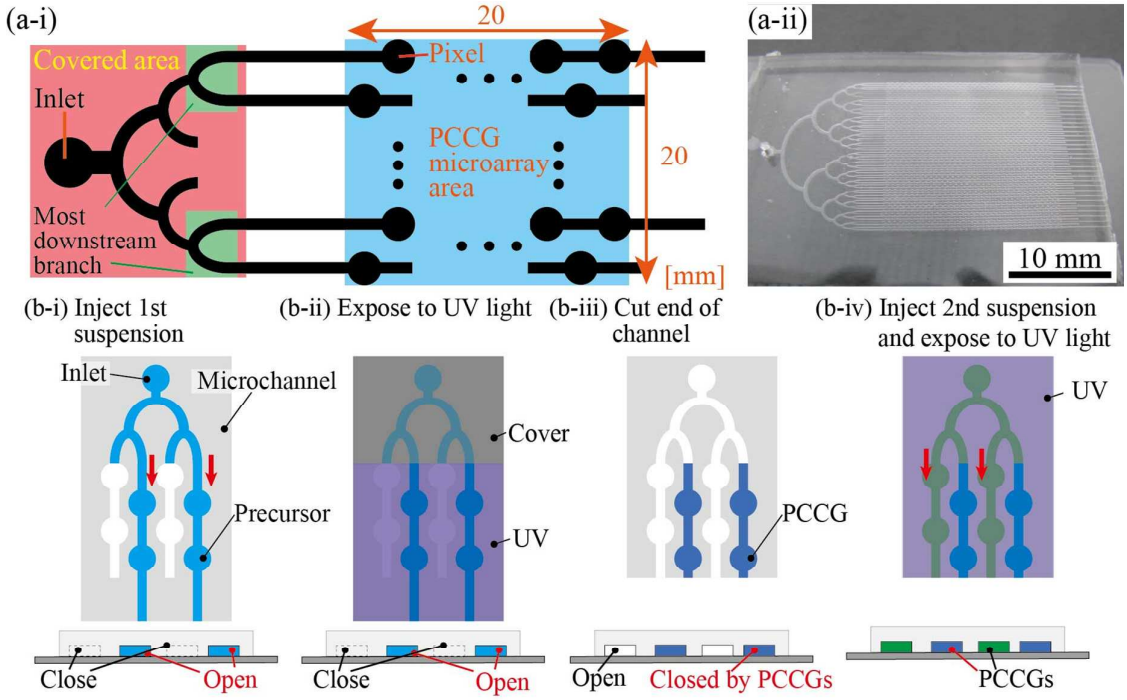


Figure 3. (a-i) Design of the microchannel employed herein. (a-ii) Image of the prepared PDMS microchannel that can pattern two types of PCCGs. (b) Schematic representation of the proposed patterning method: (b-i) The first colloidal precursor is injected into the opened channels; (b-ii) the precursor is cured by exposure to UV light, while the tournament area is covered to prevent gelation; (b-iii) the shorter channels are cut open and the remaining precursor is removed by suction; (b-iv) the second suspension is injected and cured by exposure to UV light.

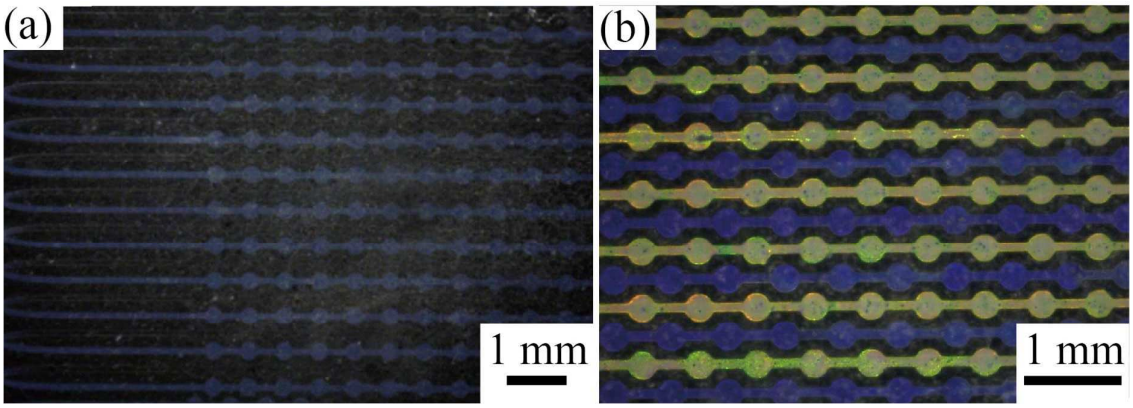


Figure 4. (a) The first precursor (diameter:110 nm, concentration: 0.24 g/mL) was selectively injected and cured; (b) the second precursor was injected and cured.

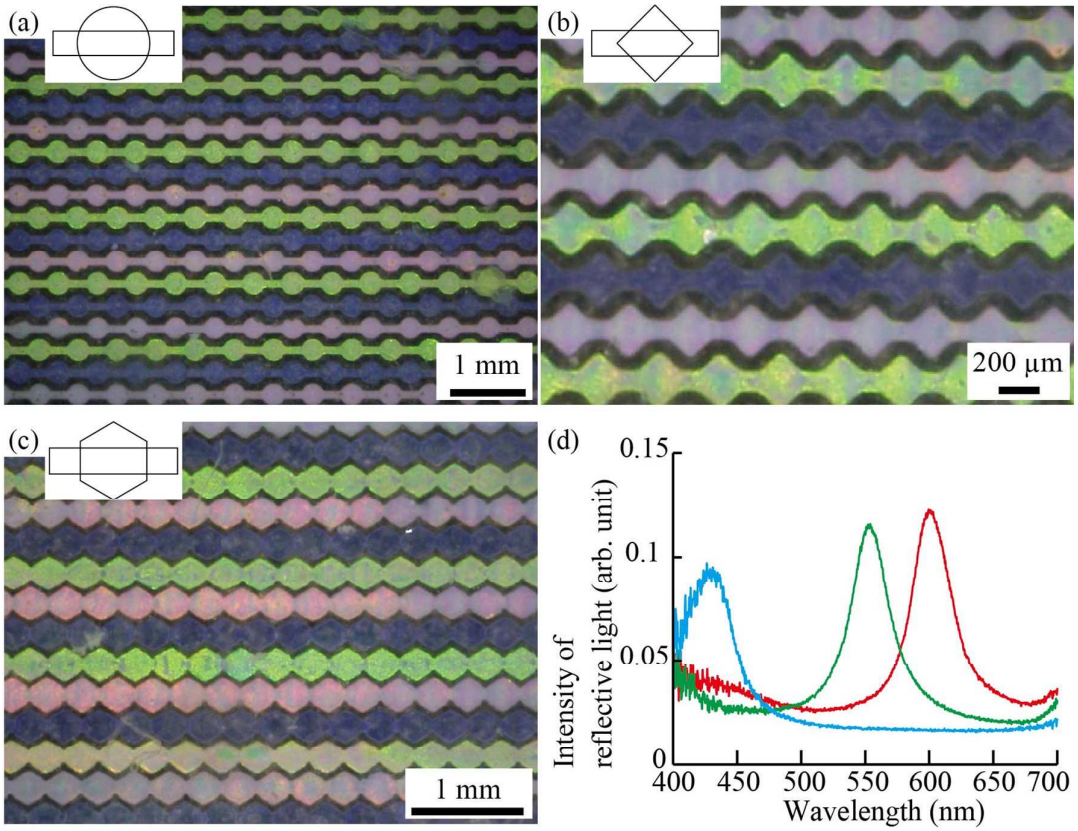


Figure 5. (a-c) Images of three patterned different types of PCCGs in the PDMS microchannels with (a) circular, (b) rectangular and (c) hexagonal pixels. (d) Vertical reflection spectra of the patterned PCCGs.

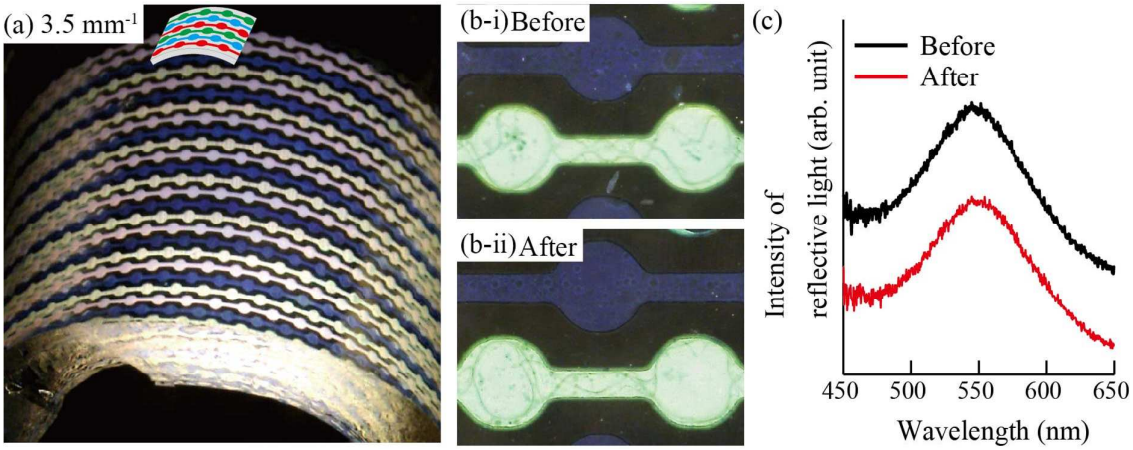


Figure 6. (a) A photographic image of the bent PCCG array. (b) Enlarged images of the PCCGs both before and after bending. (c) Vertical reflection spectra of the PCCGs both before and after bending.

Table 1. Summary of the peak reflective wavelengths for each of the numbered PCCGs outlined in part figure 2(a).

		①	②	③	④	⑤	⑥
Concentration (g/mL)		0.48	0.40	0.32	0.24	0.16	0.08
φ110 nm	Measured	UV	UV	404	470	540	N. A.
	Calculated	353	375	404	445	509	641
φ180 nm	Measured	561	620	668	IR	IR	IR
	Calculated	584	620	668	735	842	1060

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

PCCG, Photonic colloidal crystal gel, PDMS, polydimethylsiloxane, NIPAM, N-isopropylacrylamide, PEGDA, polyethylene glycol diacrylate.

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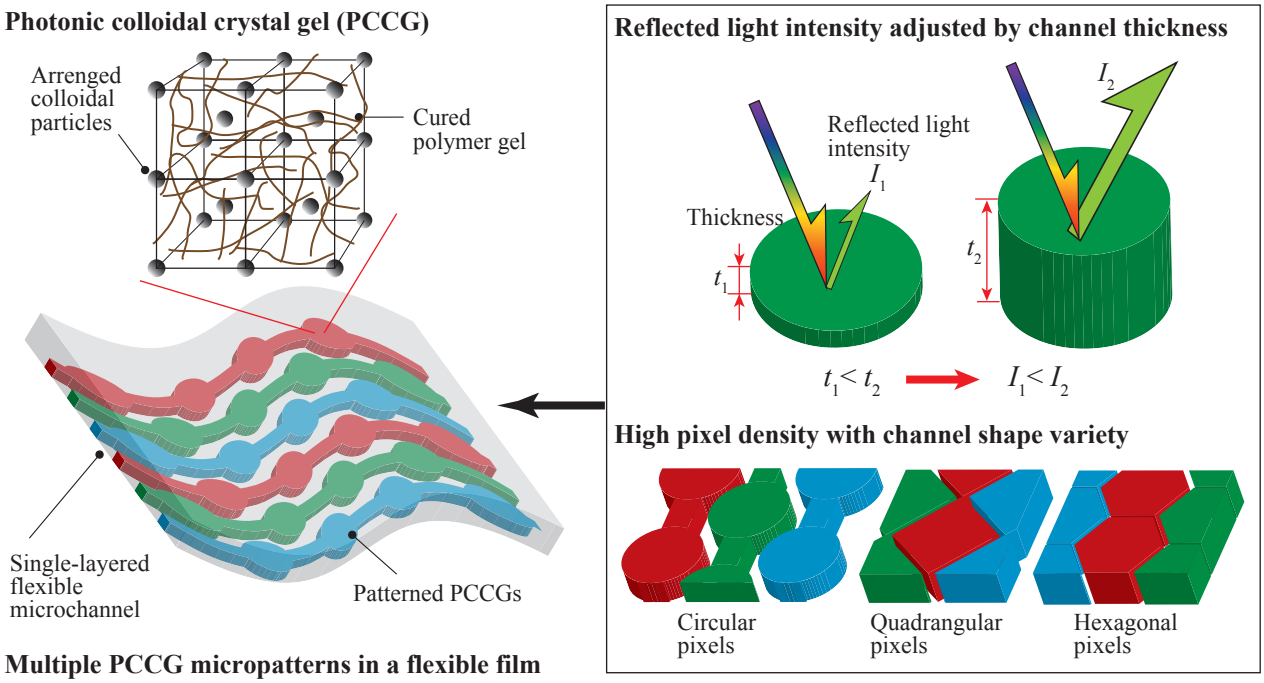
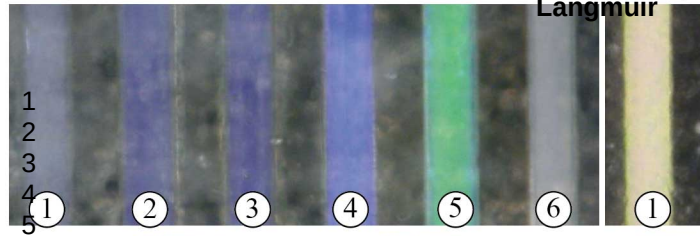
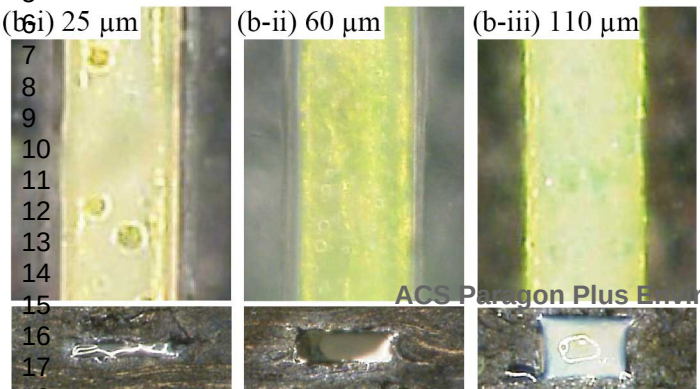
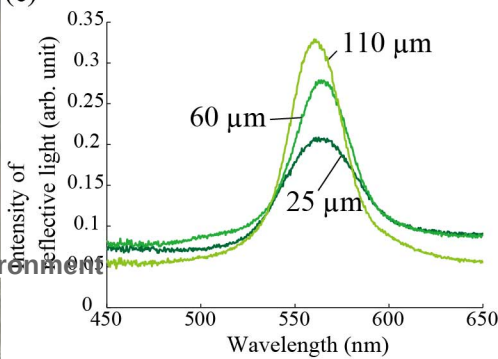

Photonic colloidal crystal gel (PCCG)
Arrenged colloidal particles
Cured polymer gel
Single-layered flexible microchannel
Patterned PCCGs
Multiple PCCG micropatterns in a flexible film
Reflected light intensity adjusted by channel thickness
Reflected light intensity
I_1
I_2
Thickness
t_1
t_2
$t_1 < t_2$
$I_1 < I_2$
High pixel density with channel shape variety
Circular pixels
Quadrangular pixels
Hexagonal pixels







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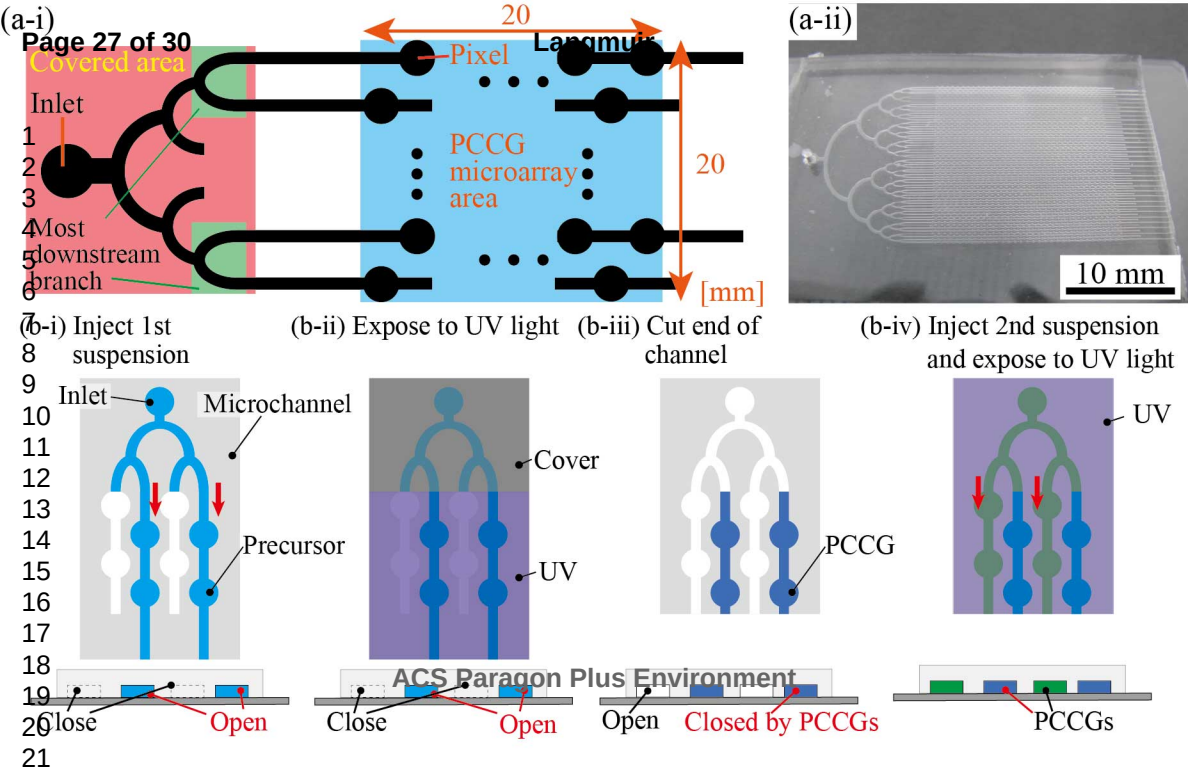

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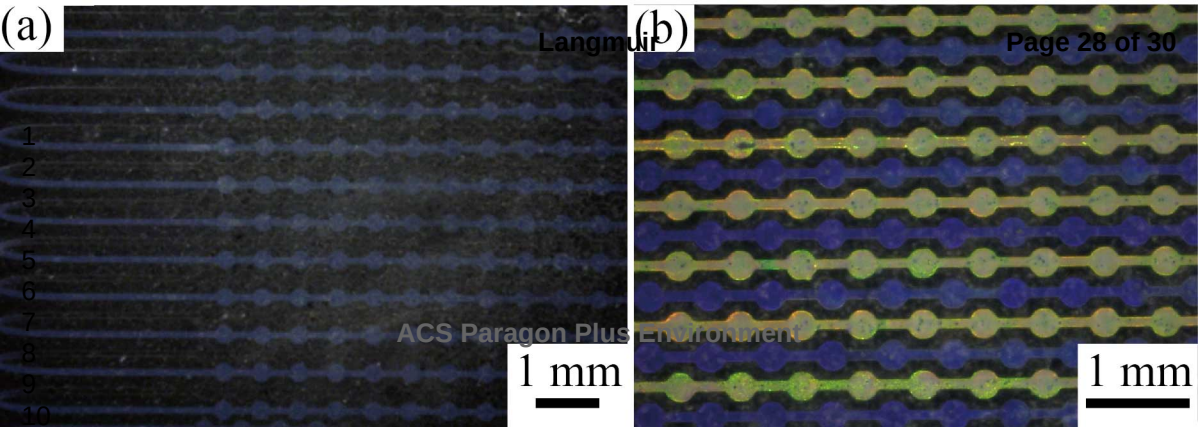

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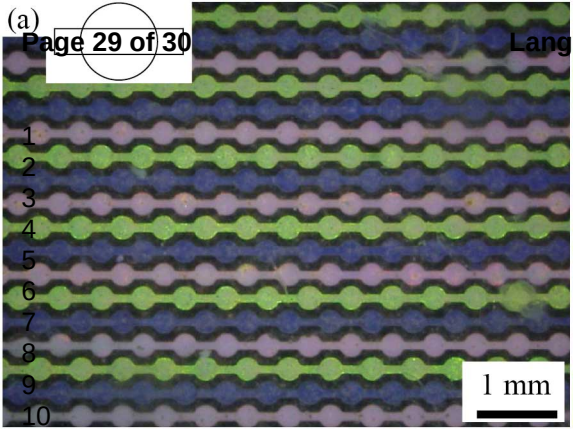

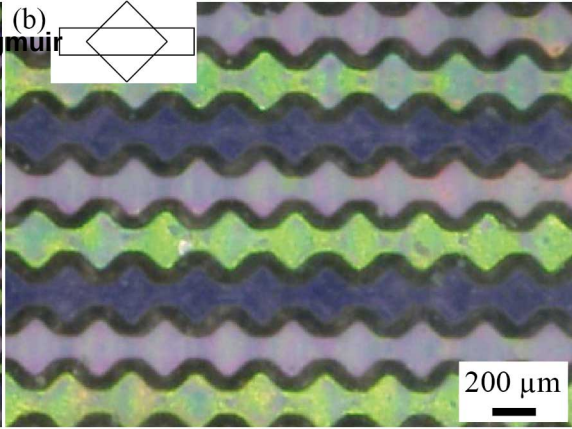

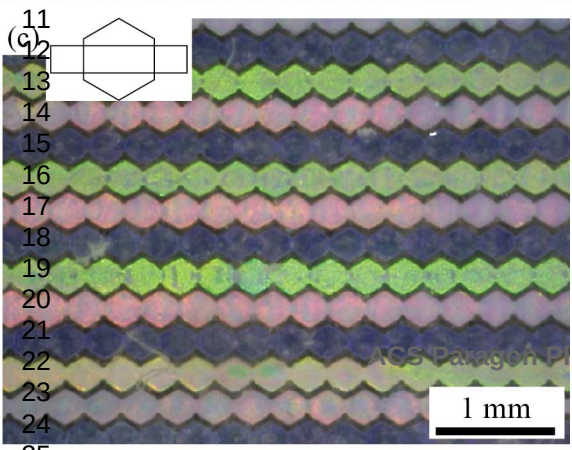

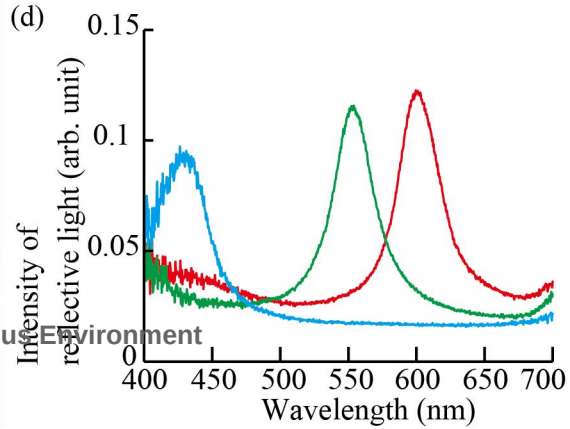

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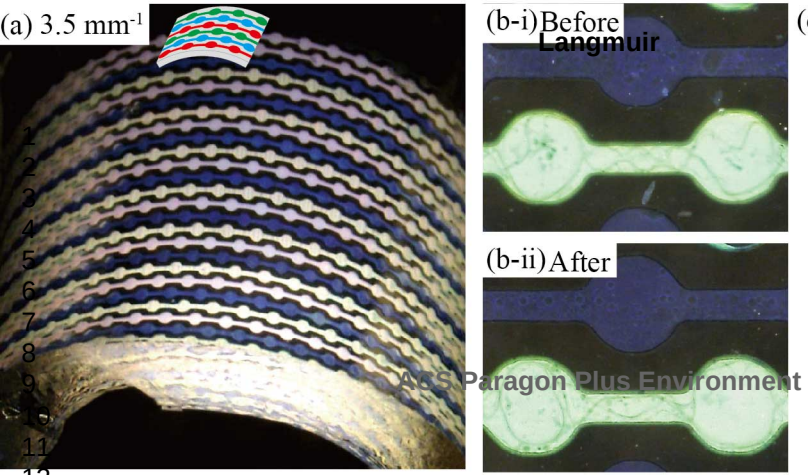

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